Conformations of Some αβ-Unsaturated Carbonyl Compounds. Part VI.[1] Comparison of Out-of-plane Olefinic CH Deformation Vibrations

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A comparison is made between the corresponding out-of-plane CH deformation modes in the compounds CH_2:CMe·CO·OX, CH_2:CHCO·OX, and MeCH:CH·CO·OX for nine different substituents X. The results provide reinterpretations of assignments, evidence of interactions between modes of a type in contrast to any expected resonance interactions, and some new considerations of conformational equilibria.

Bands assigned to fundamental olefinic CH in-phase, out-of-plane deformation vibrations (CH o.p. modes) in the i.r. spectra of substituted unsaturated compounds are particularly useful for analysis and structure determination because the absorptions are intense and occur at wavenumber values characteristic of the substituents.[2] On the basis of isotopic substitution [3] and normal co-ordinate (N.C.) calculations [4] for vinyl bromide, compounds containing a CH_2:CH– group have been seen to have three o.p. fundamentals, that at highest wavenumber corresponding to a mode in MeCH:CH– compounds and that at the next highest corresponding to one in CH_2:CMe– compounds. This correspondence is supported by the consistency of observed wavenumber values in a large number of substituted olefins.[2,5] There is no similar correspondence for the third, lowest wavenumber o.p. CH_2·CH– mode which is therefore not considered in this paper. Within this group of compounds, αβ-unsaturated carbonyl structures are of particular interest. The purpose of this paper is to show that a rigorous consideration of the assignments of o.p. CH modes clarifies and rationalizes a number of assignments and reveals unusual interactions in situations where Fermi resonance-type interactions may be expected. Certain features of o.p. CH

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[1] Part V, W. O. George, W. C. Harris, D. V. Hassid, and W. F. Maddams, preceding paper.

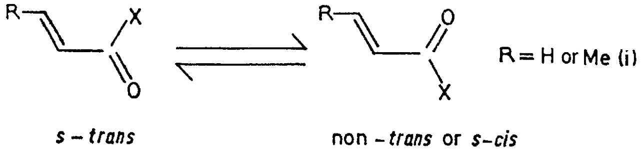
[2] W. J. Potts and R. A. Nyquist, *Spectrochim. Acta*, 1959, **15**, 679.

[3] J. Charette and M. de Hemptinne, *Bull. Class. Sci. Acad. roy. Belg.*, 1952, **38**, 934.

[4] J. R. Scherer and W. J. Potts, *J. Chem. Phys.*, 1959, **30**, 1527.

[5] D. A. Long and W. O. George, *Spectrochim. Acta*, 1963, **19**, 1717.

modes have been correlated with conformational equilibria of the type (i), and a number of these considerations have been modified.



(i)

EXPERIMENTAL

Methacrylaldehyde, methyl vinyl ketone, methyl isopropenyl ketone, methacrylic acid, methyl acrylate, methyl crotonate, acryloyl chloride, crotonyl chloride, and methacrylamide were purchased from Ralph N. Emmanual Ltd. Acrylaldehyde, crotonaldehyde, acrylic acid, crotonic acid, methyl methacrylate, and acrylonitrile were purchased from Hopkins and Williams Ltd. Acrylamide was purchased from Aldrich Chemical Co. Inc. Methacryloyl fluoride was donated by Dr. J. R. Scherer and Dr. A. Pittman of the U.S. Department of Agriculture. 2-Methylpropene, propene, and *trans*-but-2-ene were donated by Mr. A. J. Porter of Esso Research Ltd. Acryloyl fluoride and crotonyl fluoride were prepared by reactions of the corresponding chlorides with antimony trifluoride, and were redistilled. Sodium salts of acids were prepared by titration of the acids with sodium hydroxide and freeze-drying. Phenyl esters of acids were prepared by esterification with phenol and were redistilled. Crotonamide was prepared by treating crotonyl chloride with ammonia followed by evaporation.

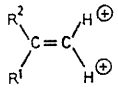
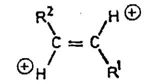
Purities were checked by recording i.r. spectra between 250 and 4000 cm^{-1} on a Perkin-Elmer 457 spectrometer, followed by comparisons with known spectra or correlations over wider regions. Wavenumber values of bands reported were measured for 2·5—5·0% solutions in carbon tetrachloride at 0·1 mm path length. Insoluble solids were studied as Nujol mulls and gases were studied at various pressures at 10 cm path length. All wavenumber values were calibrated by comparison with polystyrene and indene [6] and are expected to be accurate to ± 2 cm^{-1}.

RESULTS AND DISCUSSION

The basis of the present work is the similarity between (*a*) corresponding $CH_2\colon CHR$ and $CH_2\colon CMeR$ systems in terms of shifts induced by various substituents R on the o.p. CH_2 mode and (*b*) between corresponding $CH_2\colon CHR$ and *trans*-$R^1CH\colon CHR^2$ systems in terms of a different set of shifts induced on the o.p. *trans*-CH:CH mode by various substituents R. This is illustrated (Table 1) by comparison of the wavenumbers of the o.p. CH modes in a series of substituted olefins. The approximate forms of the o.p. CH_2 and CH:CH modes based on N.C. calculations [4] are shown for each type. For the o.p. CH_2 mode the assumption of induced shifts of -12 and $+48$ cm^{-1} by Cl and CN groups, respectively (relative to the arbitrary value of 0 for Me groups) leads to calculated values in close agreement with observed values. For the o.p. CH:CH mode an assumption of shifts of -36 and -12 cm^{-1} by the same substituents also leads to close agreement between predicted and measured values. On the basis of shift additivity, 18 hitherto unrationalized wavenumber values are empirically expressed in terms of six parameters (the Cl, CN, and Me shifts for both modes) with a mean error of less than 4 cm^{-1}.

TABLE 1

Out-of-plane bending modes in substituted olefins (ν/cm^{-1}) *

					
		o.p. CH_2 mode		o.p CH:CH mode	
R^1	R^2	Obs.	Calc.	Obs.	Calc.
H	Me	912	912	992	992
H	Cl	894	900	941	956
H	CN	955	960	972	980
Me	Me	890	890	963	963
Me	Cl	875	878	926	927
Me	CN	930	938	953	951
Cl	Cl	867	866	892	891
Cl	CN	916	926	920	915
CN	CN	985	986	942	939

* Observed values from refs. 2 and 5. ⊕ Deformation out of the plane of the molecule.

The wavenumber values of bands assigned to o.p. CH modes for a series of αβ-unsaturated carbonyl compounds are listed in Table 2. These are presented so that each of the two o.p. CH modes in the compounds $CH_2\colon CH\cdot COX$ can be compared with the corresponding mode in

TABLE 2

Out-of-plane bending modes in αβ-unsaturated carbonyl compounds

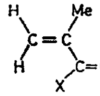
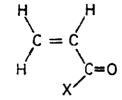
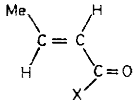
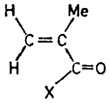
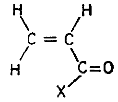
				
X	o.p. CH_2 mode	o.p CH_2 mode	o.p CH:CH mode	o.p CH:CH mode
H	938	963	987	969
Me	930	956	995	974
O^-Na^+			985	
	953	952	991	967
OH	948	973	986	971
OMe	941	967	985	970
OPh	950	967	987	969
Cl	965	974	974	962
F	954	980	996	970
NH_2	935	968	980	970

TABLE 3

Comparison of shifts of out-of-plane CH_2 bending modes

			
X	890	912	Shift difference
H	+48	+51	+3
Me	+40	+44	+4
O^-Na^+	+63	+40	−23
OH	+58	+61	+3
OMe	+51	+55	+4
OPh	+60	+55	−5
Cl	+75	+62	−13
F	+64	+68	+4
NH_2	+45	+56	+11

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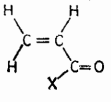
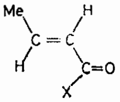
[6] I.U.P.A.C., ' Tables of Wavenumbers for the Calibration of Infrared Spectrometers,' Butterworths, London, 1961.

$CH_2{:}CMe{\cdot}COX$ and $MeCH{:}CH{\cdot}COX$. In Table 3 the shifts in the o.p. CH_2 mode induced by COX groups are compared and the shift differences between the two types are listed. In Table 4 the shift in the o.p. CH:CH modes in the two types of compound and the shift differences are also listed. For consistency, shifts are expressed in terms of the same arbitrary references as in Table 1. In both Tables 3 and 4 shift differences occur within fairly narrow ranges.

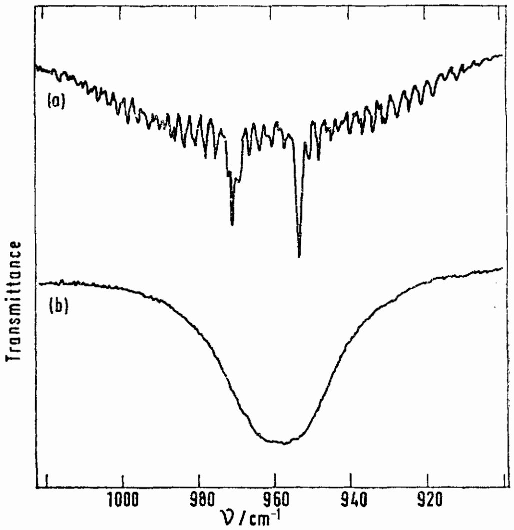
TABLE 4

Comparison of shifts of out-of-plane CH:CH bending modes

X	 992	 963	Shift difference
H	−5	+6	+11
Me	+3	+11	+8
	−7		+18
O^-Na^+	−1	+4	+5
OH	−6	+8	+14
OMe	−7	+7	+14
OPh	−8	+6	+14
Cl	−18	−1	+17
F	+4	+7	+3
NH_2	−12	+7	+19

Resonance Considerations.—A feature of some of the assignments listed in Table 2 is the apparent coincidence or near coincidence of bands assigned to the two o.p. CH modes in acrylic acid, its esters, acryloyl fluoride, acryloyl chloride, and acrylamide. A second feature is that these modes occur in the same symmetry species (a'' for the C_s point group). This means, in wave mechanical terms, that two energy levels exist with similar values and with wavefunctions of the same symmetry. These are two necessary, but not sufficient, conditions for a resonance interaction. The term ' Fermi resonance ' is normally reserved for interactions involving a fundamental and a non-fundamental, in accord with the initial [7] account of the phenomenon. Analogous interactions can occur between fundamentals and is sometimes also referred to as ' Fermi resonance ' but will be termed ' resonance ' in the present work to avoid confusion. This resonance would produce a repulsion between the levels and a wide separation of observed wavenumbers which could imply that certain assignments listed in Table 1 are in error. In addition, evidence exists for conformational equilibria in some of the compounds considered, and the possibility of additional bands from these conformers has also cast doubt on assignments in this region, particularly, as will be described later, in that certain of the band temperature dependences are unclear. To obtain information on possible resonances in the present context the spectra of acrylonitrile as a vapour [Figure (a)] and as a solution [Figure (b)] were recorded.

In acrylonitrile no axis of internal rotation about a single bond exists and therefore only a single conformer is present. The bands observed in the vapour state at 953 and 971 cm^{-1} may be assigned to the o.p. CH_2 and CH:CH modes, respectively. The mean separation of the sub-bands arising from vibration–rotation interaction is found to be 3·3 cm^{-1}. Following microwave determinations [8] of structural parameters the calculated separation of these sub-bands on the basis of the assignments proposed is 3·0 cm^{-1}. This agreement provides confirmation of these assignments for the vapour state. For the solution state the spectrum provides only one broad band in this region at 958 cm^{-1}. It must be assumed that the energy levels associated with the two o.p. CH modes have coalesced into one band. This implies an attractive interaction between levels in an opposite direction to the repulsive interaction by resonance. A probable reason for this apparent reversal is an orthogonality of wavefunction of the two levels. A requirement for resonance further to the two features already considered is non-orthogonality of wavefunction. Intuitively it appears that resonance requires an interaction between two vibrations which involve opposing motions of a common bond. Well known examples are interaction between the first harmonic of a bending mode with a fundamental stretching mode of the same bond (*e.g.* the C–O bond in carbon dioxide or the C–H bond in an aldehyde group). In wave mechanical terms this is equivalent to non-orthogonal vibrational wavefunctions. Consideration of the forms of vibration of o.p. CH modes (Table 1) reveals that these vibrations can occur independently or are orthogonal. It therefore appears that there is a tendency in some of the compounds examined for levels to become accidentally degenerate in the condensed phase, for the reasons suggested.



I.r. spectrum of acrylonitrile: (a) vapour; (b) solution in carbon tetrachloride

The assignment of the two o.p. CH modes will be considered for the various compounds $CH_2{:}CH{\cdot}COX$.

Acrylaldehyde.—The o.p. CH modes in acrylaldehyde

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[7] E. Fermi, *Z. phys.*, 1931, **71**, 250.

[8] C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, 1959, **30**, 222.

and crotonaldehyde were resolved[9] into rotational sub-bands in the vapour state; these were shown to be consistent with an *s-trans* conformation in each case. These studies confirm the assignment of the corresponding bands for the solution state (Table 2). The shift difference between the o.p. CH_2 modes in acrylaldehyde and methacrylaldehyde is +3 cm^{-1} and between the CH:CH modes in crotonaldehyde and acrylaldehyde is +11 cm^{-1}.

Methyl Vinyl Ketone.—An equilibrium between a low and a high energy conformer is well established[9] and is considered to cause splitting of the o.p. CH:CH mode in the vapour and in solution. Variable-temperature studies suggest that a band at 995 cm^{-1} is associated with a low energy (*s-trans*) conformer and a band at 985 cm^{-1} with a high energy (non-*trans* or *s-cis* conformer). The positions of these bands represent shifts of +3 and −7 cm^{-1}, respectively and, when compared with shifts of the bands assigned to the corresponding modes in ethylideneacetone, produce shift differences of +8 and +18 cm^{-1}. Both these shift differences are in line with others given in Table 3 and, therefore, represent additional confirmation of the assignments. The o.p. CH_2 mode at 956 cm^{-1} shows no splitting and the shift value differs from the corresponding shift in isopropenyl ketone by +4 cm^{-1} (Table 3).

Sodium Acrylate.—Feairheller and Katon[10] have drawn attention to difficulties in making assignments below 1000 cm^{-1} in this compound and have assigned strong i.r. bands at 952 and 991 to the CH_2 and CH:CH o.p. modes, respectively. These values are used in Table 2 and provide shift differences of −23 cm^{-1} in Table 3 and +5 cm^{-1} in Table 4. Alternatively, both modes in sodium acrylate could be assigned to the band at 991 cm^{-1}, leading to a shift difference of +16 cm^{-1}. However, there would then be no obvious assignment for the band at 952 cm^{-1}; thus the former assignment is more likely. The discrepancy in the shift difference may be attributable to the fact that the bands are measured in the solid state for an anionic species. A further consequence of these physical properties is the lack of suitable solvents for variable-temperature studies of conformational equilibria.

Acrylic Acid.—The o.p. CH_2 and CH:CH modes were assigned[10] in liquid acrylic acid to a single band at 984 cm^{-1} which narrowed sufficiently on crystallization to be resolved into two components. In the present work bands are observed at 973 and 986 cm^{-1} in solution; these provide shift differences from the corresponding methacrylate and crotonate modes in accord with the trends given in Tables 3 and 4. The complete vibrational spectrum has been interpreted in terms of a centrosymmetric dimer with strong hydrogen bonds.

Methyl Acrylate.—Strong absorptions occur at 967 and 985 cm^{-1} in solution and at 997 and 990 cm^{-1} in the solid,[11] and, although the band at 967 cm^{-1} may be held to be absent from the solid state spectrum and there is evidence for conformational equilibria, the bands at 967 and 985 cm^{-1} are assigned to the o.p. CH_2 and CH:CH modes, respectively, and it is considered that the spectra of low and high energy conformers are coincident. An unusual and confirmatory feature is the splitting of both bands into conformer pairs in the vapour state.[12] The comparisons with the corresponding modes of methyl methacrylate (Table 3) and methyl crotonate (Table 4) provide confirmation for these assignments. The band at 997 cm^{-1} in the solid corresponds to a medium intensity band at 1003 cm^{-1} in the liquid.[11] The strong band at 990 cm^{-1} in the solid is probably a superimposition of both o.p. CH modes. This coalescence on changing phase from liquid to solid resembles the coalescence of corresponding modes in the spectrum of acrylonitrile for the vapour to solution phase change.

Phenyl Acrylate.—Since the o.p. CH modes are assigned at much the same values as in the methyl ester, the effect of conjugation between the ethylenic and aromatic π-electrons is probably small.

Acryloyl Chloride.—Only two strong bands occur in the region 800—1100 cm^{-1} and it is tempting to assign the lower (936 cm^{-1}) to the o.p. CH_2 mode. However, this would lead to a shift difference of −51 cm^{-1} in Table 3 which is inconsistent with the other differences. The band at 974 cm^{-1} is therefore assigned to both the o.p. CH_2 mode (shift difference −13 cm^{-1} in Table 3) and the o.p. CH:CH mode (shift difference +12 cm^{-1} in Table 4). Katon and Feairheller[13] assign both modes to a broad overlapping band in the 970—990 cm^{-1} region of the liquid and vapour phase spectra but consider the modes to be resolved in the solid state. Splitting in lower wavenumber modes is attributed[13] to equilibria between *s-trans* and *s-cis* conformers.

Acryloyl Fluoride.—Koster[14] has provided n.m.r. evidence for an equilibrium between a low energy *s-trans* form and a high energy *s-cis* form. In solution prominent bands occur at 980 and 996 cm^{-1}. A slight temperature dependence of these was used by Carlson *et al.*[15] to assign this pair to the o.p. CH:CH mode in the high and low energy conformers, respectively. In the i.r. spectrum of the solid an intense band was reported at 1000 cm^{-1} with a shoulder at 990 cm^{-1}. It was concluded[15] that the i.r. evidence for conformational equilibria was only meagre. Because of the possibility of a multiplicity of bands owing to conformational equilibria, assignments are best made by comparison with the corresponding modes in methacryloyl fluoride and crotonyl fluoride. The o.p. CH_2 mode was previously assigned at 800 cm^{-1} in acryloyl fluoride[15] which, when compared with the corresponding band in methacryloyl fluoride (954 cm^{-1} in the present

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[9] A. J. Bowles, W. O. George, and W. F. Maddams, *J. Chem. Soc. (B)*, 1969, 810.

[10] W. R. Feairheller and J. E. Katon, *Spectrochim. Acta*, 1967, **23A**, 2225.

[11] W. O. George, D. V. Hassid, and W. F. Maddams, *J.C.S. Perkin II*, 1972, 400.

[12] A. J. Bowles, W. O. George, and D. B. Cunliffe-Jones, *J. Chem. Soc. (B)*, 1970, 1070.

[13] J. E. Katon and W. R. Feairheller, *J. Chem. Phys.*, 1967, **47**, 1248.

[14] D. F. Koster, *J. Amer. Chem. Soc.*, 1966, **88**, 5067.

[15] G. L. Carlson, W. G. Fateley, and R. E. Witkowski, *J. Amer. Chem. Soc.*, 1967, **89**, 6437.

work) would lead to a shift difference of -176 cm^{-1}. In the present work the o.p. CH_2 mode in acryloyl fluoride is assigned at 950 cm^{-1}, leading to a shift difference of $+4$ cm^{-1} (Table 3), in close agreement with the other values. This confirms the revised assignments. There are two possibilities for the assignment of the o.p. CH:CH mode. First, it may be coincident with the o.p. CH_2 mode at 980 cm^{-1} to give a shift difference in Table 4 of $+19$ cm^{-1}. Secondly, it may be assigned to the band at 996 cm^{-1} to give a shift difference of $+3$ cm^{-1}. These values are at opposing extremes of the range quoted and the latter is preferred. In the solid phase these modes are considered to coalesce completely (or partly) at 1000 cm^{-1} (shoulder at 990 cm^{-1}) in a manner similar to the coalescence observed for the same modes in acrylonitrile, methyl acrylate, and acryloyl fluoride. These confirm the paucity of i.r. evidence for conformational equilibria in acryloyl fluoride.

Acrylamide.—The assignments of the o.p. CH modes are consistent with those in methacrylamide and crotonamide. These bands may serve as a structural probe in studies of amide conformations.

The present work therefore provides a basis for comparing assignments of a large number of compounds within particular classes and gives evidence for choosing between alternatives. Information on the nature of the modes based on empirical comparison is consistent with the same information based on normal co-ordinate calculations. This information is particularly valuable for molecules which may be involved in conformational equilibria.

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